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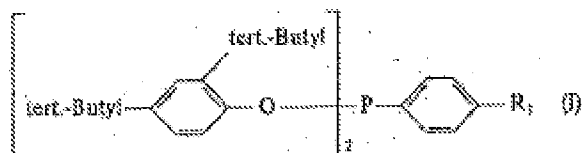
STABILIZERS FOR POLYMER ORGANIC COMPOUNDS
[Stabilisatoren für polymere organische Verbindungen]

Jean-Paul Kehrli et al.

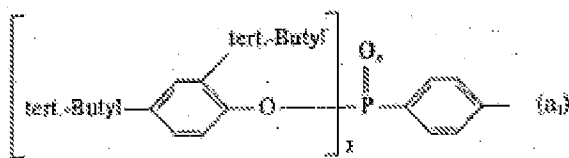
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It was found that polymer organic compounds can be very effectively stabilized, especially against yellowing and the decomposition that subsequently occurs, by mixing in a stabilizer consisting of 30-80 wt% of a compound of formula I



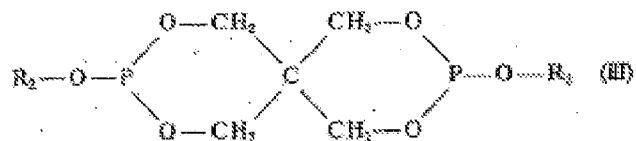
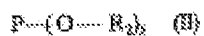
in which R_1 is hydrogen, methyl, unsubstituted phenyl or a group of the formula a₁



in which n is zero or 1,

and 20-70 wt% of an organic phosphite compound.

Preferred phosphites corresponding to formula II or III,



in which all R₂ are independently linear or branched C₁₋₂₂ alkyl or optionally phenyl carrying up to 3 linear or branched C₁₋₄ alkyl groups, preferably methyl and/or tert-butyl.

Especially preferred organic phosphites are, for example, tris(2,4-di-tert-butylphenyl) phosphite, tris(nonylphenyl) phosphite, trilauryl phosphite, bis(2,6-di-tert-butyl-4-methylphenyl)pentaerythryl diphosphite, bis(2,4-di-tert-butylphenyl)pentaerythryl diphosphite and distearyl pentaerythryl diphosphite.

These stabilizer mixtures are generally used in amounts from 0.01-1.0, preferably 0.05-0.3 wt%, with respect to the polymer organic compounds that are to be stabilized.

Preferably, the stabilizers consist of 40-70, especially 40-60 wt% of a compound of formula I and 60-30, preferably 60-40 wt% of an organic phosphite compound.

The stabilizers in accordance with the invention can additionally contain antioxidants, for example, sterically-hindered phenolic antioxidants, sulfur-containing or aminoryl [sic; aminoaryl] antioxidants. The latter compounds are in general present in amounts between 0.5 and 2 parts by weight per part by weight phosphorus-containing stabilizers.

Preferred phenolic antioxidants are, for example: octadecyl-3-(3',5'-di-tert-butyl-4'-hydroxyphenyl) propionate, pentaerythryltetrakis-3-(3',5'-di-tert-butyl-4'-hydroxyphenyl) propionate, 1,3,5-tris(3',5'-di-tert-butyl-4'-hydroxyphenyl) isocyanurate, 1,1,3-tris(5'-tert-butyl-4'-hydroxy-2'-methylphenyl)butane, 1,3,5-tris(tris(3',5'-di-tert-butyl-4'-hydroxybenzyl)mesitylene and ethylene glycol bis[3,3-(3'-tert-butyl-4'-hydroxyphenyl) butyrate].

Preferred aminoaryl antioxidants are, for example: N,N'-dinaphthyl-para-phenylenediamine and N,N'-hexamethylenebis(3,5-di-tert-butyl-4-hydroxyphenyl)propionamide.

Preferred sulfur-containing antioxidants are, for example: ditiidecyl 3,3-thiodipropionate, dilauryl 3,3'-thiodipropionate, dilauryl 3,3'-thiodipropionate [sic], distearyl 3,3'-thiodipropionate, methanetetakis(methylene-3-hexylthiopropionate) and dioctadecyldisulfide.

Another possibility as additive to the stabilizers in accordance with the invention is, for example, α -tocopherol (vitamin E).

The stabilizers in accordance with the invention are preferably suitable for all polyolefins (for example, high- and low-pressure polyethylene, polypropylene), polyisobutylene, poly-4-methylpentene and the copolymers of these plastics. They are also effective for stabilizing polystyrene (and its copolymers), ABS, polyvinyl acetate, polyvinyl alcohol, polyacetate (POM), polyacrylates, polyacrylonitrile, polyacrylamide, PVC, polyvinylidene chloride, polyamides, polyesters, polyethers, polythioethers and thioplastics, polycarbonates, polyurethane, cellulose derivatives, maleic acid, melamine, phenol, aniline, furan, carbamide, epoxide and silicon resins.

The polymer organic materials modified in accordance with the invention can also additionally contain flame retardants, antistatic agents, UV absorbers, UV stabilizers, plasticizers, nucleation agents, metal deactivators, biocides, fillers and pigments.

The stabilizers used in accordance with the invention can be mixed into the polymer organic compounds at each stage in their processing: before, during or after the polymerization or polycondensation. They can be used as is, in solid or molten form, in solution (preferably as a 10-80 wt% solution), for example as a 10-90 wt% concentrate (master batch) with the plastic that is to be stabilized or with a plastic that is compatible with it.

In general, the stabilizers used in accordance with the invention are incorporated into the melt of the material to be stabilized, which is carried out, for example, in an extruder or a melt spinning machine.

Then the plastics are processed, for example, to films, tubes, fibers, threads, foams and other molded articles.

The stabilizers used in accordance with the invention are especially suitable for fibers and films of polypropylene.

Example 1

A solution of

1.0 g calcium stearate,

1.0 g pentaerythryltetrakis-3-(3',5'-di-tert-butyl-4'-hydroxyphenyl) propionate,

0.4 g tetrakis(2,4-di-tert-butylphenyl)-4,4'-diphenylene diphosponite,

0.4 g tris(2,4-di-tert-butylphenyl) phosphite and

0.2 g bis(2,4-di-tert-butylphenyl)diphenyl phosphite

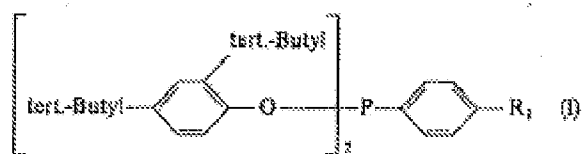
is prepared in 25 mL acetone. This solution is added to 1000 g polypropylene powder and treated for 5 min in a mixer at 400 RPM. Then the mixture is dried for 30 min at 50°C, put into a Göttfert extrusimeter (with a 20 mm screw, compression 1:3, diameter/length ratio 1:20) and, heated to 270°C, extruded several times. After each extrusion, the melt flow index (MFI) is measured at 230°C/2.16 kp and evaluated as a characteristic of the stabilizing effect.

Examples 2-4

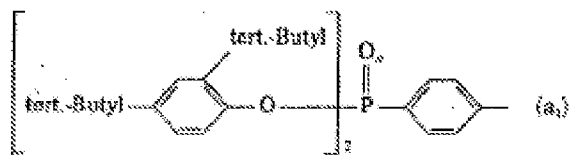
Instead of the 0.4 g tris(2,4-di-tert-butylphenyl) phosphite, one uses only 0.2 g of this compound and (Example 2) 0.2 g tris(nonylphenyl) phosphite, (Example 3) 0.2 g of a 4:6 (parts by weight) mixture of α -tocopherol and tris(nonylphenyl) phosphite, and (Example 4) 0.2 g of a 2:4:4 (parts by weight) mixture of α -tocopherol, ditridecyl 3,3'-thiodipropionate and trilauryl phosphite.

Claims

1. Stabilizers for polymer organic compounds that contain 30-80 wt% of a compound of formula I



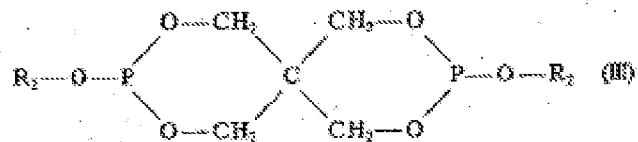
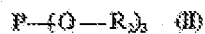
in which R_1 is hydrogen, methyl, unsubstituted phenyl or a group of the formula a_1



in which n is zero or 1,

and 20-70 wt% of an organic phosphite compound.

2. Stabilizers for polymer organic compounds as in Claim 1, in which the organic phosphite compound of formula II or III corresponds to



in which all R_2 are independently linear or branched C_{1-22} alkyl or phenyl optionally carrying up to 3 linear or branched C_{1-4} alkyl groups, preferably methyl and/or tert-butyl.

3. Stabilizers for polymer organic compounds as in Claim 1 or 2, which contain 40-70, especially 40-60 wt% of a compound of formula I and 60-30, preferably 60-40 wt% of an organic phosphite compound.

4. Stabilizers for polymer organic compounds that additionally contain 0.5-2 parts by weight of one or more known antioxidants per part by weight of the stabilizer mixture as in one of the preceding claims.

5. A concentrate of stabilizers as in one of the preceding claims that contains 10-80 wt% of a mixture of stabilizers and 90-20 wt% of one or more solvents of the polymer organic compound to be stabilized, or a compound that is compatible with it, and optionally, antioxidants.

6. Polymer organic compounds containing at least one stabilizer mixture as in one of Claims 1-3, in amounts of 0.01-1.0, preferably 0.05-0.3 wt%.